Growth of Needle-like α-FeO (OH) Particles by Air Oxidation of Aqueous Suspensions Containing Iron (II) Precipitates (Commemoration Issue Dedicated to Professor Toshio TAKADA On the Occasion of His Retirement)

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The conditions were investigated for the growth of needle-like particles of α-FeO(OH) by air oxidation at 40°C of $Fe(OH)_2$ suspensions. The particle sizes of each α-FeO(OH) sample were estimated from the BET surface area, X-ray powder diffraction, and microscopic examinations. The particle growth during oxidation was accelerated with increasing the concentrations of both excess NaOH and $Fe(OH)_2$ in the starting suspension, whereas in the presence of NH_4^+ ion with increasing the $Fe(OH)_2$ concentration in the neutral suspension. The Fe_3O_4 and γ-Fe_2O_3 samples, each consisting of needle-like particles, were obtained by heat treatments of the α-FeO(OH) samples with the narrow distribution of particle size and shape, and their magnetic properties were measured at room temperature.

KEY WORDS: Air Oxidation/ Needle-like particle/ Particle growth/ α-FeO(OH)/ Fe_3O_4/ γ-Fe_2O_3/ Coercivity/

INTRODUCTION

Either a neutral or an alkaline suspension of $Fe(OH)_2$ is obtained by mixing aqueous solutions of NaOH and iron(II) salt as $FeSO_4$ or $FeCl_2$ with less or greater than 1.0 in the mol ratio of 2NaOH/Fe(II). The precipitate of $Fe(OH)_2$ in the suspension directly or indirectly transforms by air oxidation into the precipitate of FeO(OH) or Fe_3O_4 depending on the oxidation conditions. At oxidation temperatures lower than those at which Fe_3O_4 is formed, α-FeO(OH) is directly formed in the alkaline suspension, whereas α- or γ-FeO(OH) is formed via green rusts in the neutral suspension, depending on the kind of acid anion present.[1] The α- or γ-FeO(OH) sample thus obtained consists respectively of needle-like or flaky particles.

The needle-like α-FeO(OH) particles have been widely used as the starting material for the magnetic recording media. The coercive force, Hc, of the γ-Fe_2O_3 or Fe_3O_4 particles has been known to become greater with increasing the shape anisotropy.[2] Such ferromagnetic particles could be prepared by careful heat-treatments of the needle-like α-FeO(OH) particles. The use of $FeSO_4$ as an iron(II) salt and keeping the suspension at 40°C were favorable for the formation of α-FeO(OH) by oxidation.

This paper deals with oxidation conditions for the growth of needle-like α-

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FeO(OH) particles and the magnetic properties of the ferromagnetic particles prepared from the α-FeO(OH) particles.

EXPERIMENTAL

Neutral and alkaline suspensions (each 3 dm^{-3}) of $Fe(OH)_2$ were prepared by mixing an aqueous solution of $FeSO_4$ and that of NaOH (both of an analytical grade) in various $2Na^+/Fe(II)$ ratios(R). These suspensions were heated to 40°C and then oxidized at 40°C by bubbling CO_2-eliminated air into them at various constant rates. Oxidation in the neutral supsensions with $R<1$ was stopped as soon as the pH dropped below 5, whereas oxidation in the alkaline suspensions with $R>1$ was continued until the $Fe(OH)_2$ precipitate completely disappeared. The oxidation method for the suspensions was the same as that previously reported.[1] The neutral suspensions with $R<1$ were also prepared by mixing an aqueous solution of $FeSO_4$ and either of NH_4OH or Na_2CO_3 one.

To investigate the transformation into α-FeO(OH) in the course of oxidation, a 40–50 cm^3 sample was taken several times from the suspensions during oxidation. After sampling, the filtered precipitate in a muddy form was subjected to X-ray and electron microscopic examinations. The oxidation products were filtered, well washed with water, treated with acetone and then dried at 70°C in air. The powdery samples thus obtained were examined by X-ray powder diffraction using Mn filtered FeKα radiation, electron microscopic observation and BET surface area determination using nitrogen.

RESULTS AND DISCUSSION

When excess NaOH was added to a $FeSO_4$ solution, the alkaline and whitish suspension was obtained. The whitish precipitate in the suspension, consisting of extremely fine particles of $Fe(OH)_2$, was observed to gradually change to a yellowish precipitate by oxidation. The ultimate product was a yellowish precipitate, consisting of needle-like particles of α-FeO(OH) when suitable concentrations of excess NaOH and of $FeSO_4$ and an air flow rate were selected. The increases in the excess NaOH concentration and in the air-flow rate and the decrease in the $Fe(OH)_2$ concentration in the starting suspensions were known to be favorable for the formation of α-FeO(OH) by oxidation.

A number of the alkaline suspensions, varying in the concentrations of $FeSO_4$ and of excess NaOH, were prepared and oxidized by bubbling air into at a rate of 500 dm^3/h. The rate of formation of α-FeO(OH) by oxidation decreased as the excess NaOH concentration was increased.

The needle-like particles of greater than 1 μm in length, which were often seen in the photographs of each sample, were formed by the cohesion of several needle-like particles in the longitudinal direction. α-FeO(OH) particles are known to grow along the [001] direction of an α-FeO(OH) crystal.[3,4] The needle-like particles were found by electron microdiffraction to lie on the (100) face and occasionally on the (010) face.

The mean axial (length to width) ratio, k, of the particles was measured for approximately 20–30 particles in each sample. It was found that α-FeO(OH) particles, prepared from the alkaline suspension by oxidation, have 10 or greater in k. The mean particle size, d[110], was estimated from the line broadening of the X-ray diffraction peak for the (110) face of α-FeO(OH) crystal structure, assuming that the particles contained no crystal strain. The mean particle size, d[100] (=d[110] cos 24°4′), in the [100] direction was caluculated from the size, d[110]. The mean size, d[010], for the [010] direction was estimated, assuming that the needle-like particle was rectangular with k=10 in shape, as follows;

$$\rho S/2 = (d[100])^{-1}+(d[010])^{-1}+(d[010]\cdot k)^{-1}$$

where ρ(=4.28) is the specific density of α-FeO(OH) crystal and S the BET surface area (m^2g^{-1}).

Transmission electron micrographs and the mean particle sizes of typical α-FeO(OH) samples, prepared from the alkaline suspensions, containing 0.12M(M=mol dm^{-3}) $Fe(OH)_2$ and different concentrations of the excess NaOH, are given in Fig. 1 and Table 1, respectively. The values of mean particle volume, V(=d[100]·d[010]·d[010]k), for the α-FeO(OH) samples are plotted against the concentrations of $Fe(OH)_2$ in the starting suspension at 0.42, 1.25 and 2.5M excess NaOH in Fig. 2.

Electron microscopic examination showed that the growth of needle-like particles by oxidation was promoted with incresing both the concentrations of excess NaOH

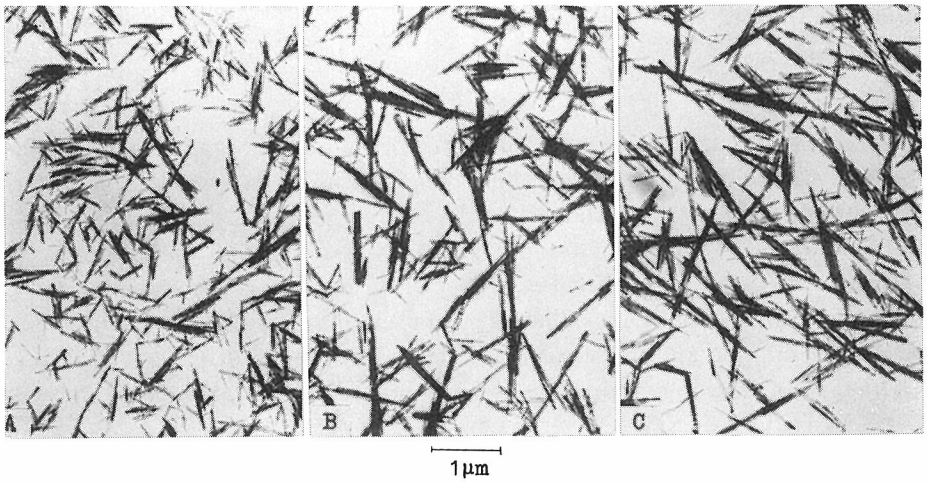

Fig. 1. Transmission electron micrographs (TEM) of α-FeO(OH) samples (Table 1).

Table 1. α-FeO(OH) samples prepared by air oxidation of alkaline suspensions containing 0.12 M $Fe(OH)_2$ and one of 0.42 (A), 1.25 (B), or 2.5 M excess NaOH(C).

Sample	S/m^2g^{-1}	d[100]/μm	d[010]/μm	$V/10^{-16}$ cm^3
A	47.2	0.018	0.024	1.0
B	41.4	0.021	0.027	1.5
C	31.2	0.026	0.039	3.9

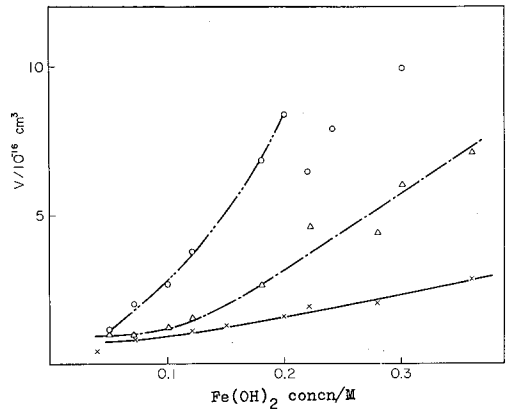

Fig. 2. Plot of the V values of α-FeO(OH) samples as a function of the $Fe(OH)_2$ concentration in the starting suspensions containing 0.42(×), 1.25(△) and 2.5M excess NaOH(○).

and $Fe(OH)_2$ in the starting suspension. When the $Fe(OH)_2$ concentration in the starting suspension, containing 2.5M excess NaOH, was increased greater than 0.2M, the particle size of the α-FeO(OH) samples obtained decreased and increased with the $Fe(OH)_2$ concentration as a result of the formation of fine needle-like particles and their subsequent growth by oxidation.

Neutral suspensions, containing 0.24M Fe(II), were prepared in the range $0.1 \leq R \leq 0.6$. On adding a solution of NaOH or NH_4OH to a $FeSO_4$ solution, a whitish precipitate with a tint green was formed. The neutral suspensions were oxidized by bubbling air into at 200 dm^3/h. A dark green precipitate, consisting of hexagonal, plate-like particles with the same crystal structure as that of green rust II,[5] appeared upon oxidation. With the progress of oxidation the formation of the nonferromagnetic, yellowish precipitate, consisting of extremely fine needle-like particles of α-FeO(OH), took place at pH 6.5–6.0 in the presence of green rust II. As the precipitate of green rust II transformed completely by oxidation into α-FeO(OH) with or without Fe_3O_4 the pH sharply dropped to 5 or less. Under these conditions, the R value at which Fe_3O_4 was intermingled in the oxidation products was 0.5 or greater. The time duration needed for the transformation into α-FeO(OH) by oxidation was apporoximately proportional to the R value.

It has been known that the presence of carbonate ion in the neutral suspension facilitates the formation of α-FeO(OH) by oxidation.[6,7] When a solution of $NaCO_3$ was added to a solution of $FeSO_4$ in the $R \leq 0.95$ range, a whitish precipitate was formed, consisting of fine crystalline particles of $FeCO_3$. In the case of $R \geq 0.6$, the formation of α-FeO(OH) proceeded at pH 6.5–6.0 in the presence of $FeCO_3$ with or without green rust II by oxidation, and the distributions of the particle size and shape of the resulting samples with $38 \leq S \leq 39$ m^2g^{-1} were found to become wider with increasing the R values.

Electron microscopic examination showed that the α-FeO(OH) particles, ob-

tained in the presence of Na^+ ions from the suspensions with $R \leq 0.45$, were extremely elongated as compared with those obtained in the presence of NH_4^+ ion and that the presence of CO_3^{2-} ion retarded the formation of the Y and X shaped, fine particles. The [010] values of the α-FeO(OH) samples were caluculated as described previously using k=5 for the samples obtained in the presence of NH_4^+ ion and k=10 for those obtained in the absence of NH_4^+ ion.

TEM and properties of typical samples, prepared from neutral suspensions with R=0.45, containing 0.24M $FeSO_4$, are given in Fig. 3 and Table 2, respectively.

To investigate the effect of the growth of α-FeO(OH) particles by oxidation on the $Fe(OH)_2$ or $FeCO_3$ concentration in the neutral suspension, the following experiments were carried out. The neutral suspensions were prepared by mixing solutoins of $FeSO_4$ and either NaOH or Na_2CO_3 at R=0.35, varying the concentrations of Fe(II) in the range 0.1–0.6M (corresponding to the concentrations 0.035–0.21M $Fe(OH)_2$ or $FeCO)_3$ and were subjected to oxidation.

The V values of the α-FeO(OH) samples are plotted against the concentration of $Fe(OH)_2$ or $FeCO_3$ for three kinds of suspensions with $R \leq 0.45$ in Fig. 4. The growth of α-FeO(OH) particles by oxidation is promoted with increasing the $Fe(OH)_2$ concentration in the presence of NH_4^+ ion. In the case where the concentration of $Fe(OH)_2$ or $FeCO_3$ was increased greater than 0.12M the particle growth by oxidation was found in the absence of NH_4^+ ion to be less dependent on the con-

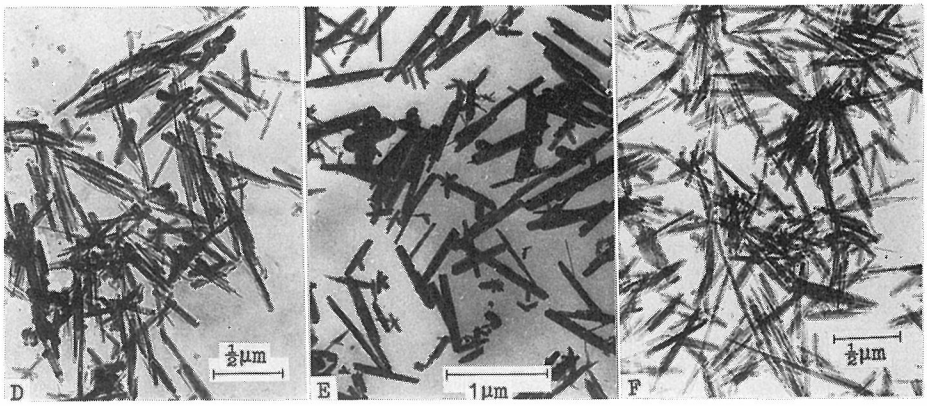

Fig. 3. TEM of α-FeO(OH) samples (Table 2).

Table 2. α-FeO(OH) samples prepared by air oxidation of neutral suspensions with R=0.45, containing 0.108 M $Fe(OH)_2$ (D and E) or $FeCO_3$(F).

Sample	S/m^2g^{-1}	d[100]/μm	d[010]/μm	$V/10^{-16}$ cm^3
D	41.2	0.019	0.031	1.8
E	25.3	0.026	0.078	7.9
F	39.0	0.017	0.045	3.5

Samples D and E were prepared in the presence of Na^+ and NH^+_4 ions, respectively.

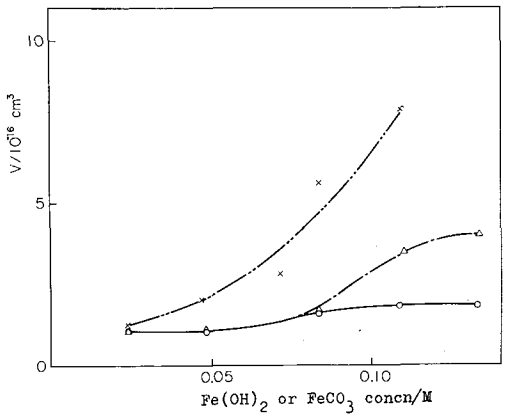

Fig. 4. Plot of the V values of α-FeO(OH) samples as a function of the concentration of iron(II) precipitates in the starting suspensions. NaOH(○), NH_4OH(×) and Na_2CO_4(△) used as precipitants.

centration.

The α-FeO(OH) samples with the comparatively narrow distribution of particle size and shape were selected from the numerous samples which had been prepared from the alkaline suspensions and then directly reduced in hydrogen at 330°C to Fe_3O_4. A portion of each Fe_3O_4 sample was oxidized in air at 190°C to γ-Fe_2O_3. The ferromagnetic samples thus obtained were packed into brass cylinders 0.6 cm in diameter and 0.2 cm in height with packing densities, P (g cm^{-3}), 0.6–0.8. Magnetic measurements with these samples were carried out at room temperature in a magnetic field up to 10 kOe (1kOe=$10^6/4\pi$A m^{-1}) using a vibrating sample magnetometer. Since the Hc values of each sample with P>0.5 were dependent on the P, the Hc values of the samples were normalized at P=0.5 by using the same method as that has previously been described.[8] The properties of the ferromagnetic samples obtained from typical three α-FeO(OH) samples with S=23 (Fig. 5(a)), 30(b) and 37 m^2g^{-1}(c) are given in Table 3, and TEM of the samples before and after the reduction are shown in Fig. 5.

The mean particle size of each Fe_3O_4 sample estimated from the S value depends on that of the α-FeO(OH) sample used. The mean particle size as well as the par-

Table 3. Properties of Fe_3O_4 and γ-Fe_2O_3 samples A, B and C prepared from α-FeO(OH) samples (a), (b) and (Fig. 5 (c)) respectively.

Sample	Fe_3O_4			γ-Fe_2O_3	
	S/m^2g^{-1}	*M/emu g^{-1}	Hc/Oe	M/emu g^{-1}	Hc/Oe
A	15.7	85	435	75	427
B	19.1	85	454	76	446
C	21.2	84	437	74	428

* 1 emu $g^{-1}=4\pi 10^{-4}$ ρWb m^{-2} where ρ=specific gravity in units of 10^3 kg m^{-3}.

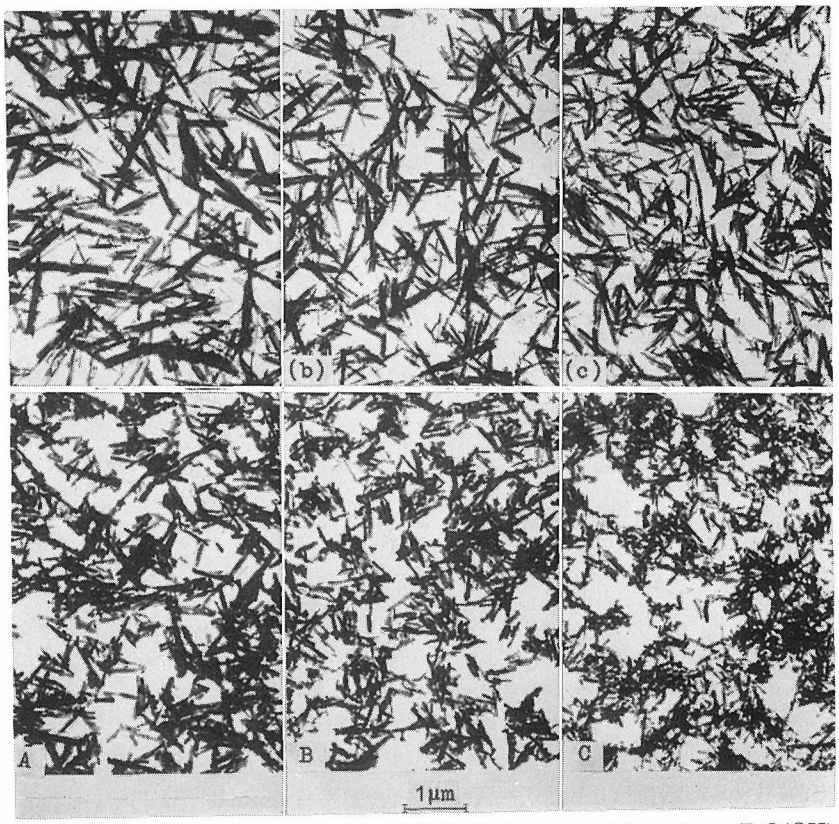

Fig. 5. TEM of Fe_3O_4 samples A, B and C (Table 3) prepared from the α-FeO(OH) samples (each uper position).

ticle shape was almost unchanged with oxidation to γ-Fe_2O_3. The Hc values of the samples prepared from the α-FeO(OH) samples with $S \leq 23$ and $S \geq 37$ m^2g^{-1} become smaller than those of the samples prepared from the α-FeO(OH) sample with $S=30$ m^2g^{-1} corresponding to $V=4\times10^{-16}$ cm^3 (Fig. 5(b)). This was due to the formation of microscopic pores in each needle-like particle (for $S \leq 23$) or the decrease in the shape anisotropy (for $S \geq 37$ m^2g^{-1}).

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